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*Published in:*  
Physical Review Letters

*Link to article, DOI:*  
[10.1103/PhysRevLett.93.146103](https://doi.org/10.1103/PhysRevLett.93.146103)

*Publication date:*  
2004

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Lopez, N., Lodziana, Z., Illas, F., & Salmeron, M. (2004). When Langmuir is too simple: H-2 dissociation on Pd(111) at high coverage. *Physical Review Letters*, 93(14), 146103.  
<https://doi.org/10.1103/PhysRevLett.93.146103>

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## When Langmuir Is Too Simple: $H_2$ Dissociation on Pd(111) at High Coverage

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(Received 8 October 2003; published 29 September 2004)

Recent experiments of  $H_2$  adsorption on Pd(111) [T. Mitsui *et al.*, *Nature* (London) **422**, 705 (2003)] have questioned the classical Langmuir picture of second order adsorption kinetics at high surface coverage requiring pairs of empty sites for the dissociative chemisorption. Experiments find that at least three empty sites are needed. Through density functional theory, we find that  $H_2$  dissociation is favored on ensembles of sites that involve a Pd atom with no direct interaction with adsorbed hydrogen. Such active sites are formed by aggregation of at least 3 H-free sites revealing the complex structure of the “active sites.”

DOI: 10.1103/PhysRevLett.93.146103

PACS numbers: 68.43.Bc, 68.37.Ef, 82.45.Jn, 82.65.+r

Under operating conditions, heterogeneously catalyzed chemical reactions take place on surfaces with dense layers of adsorbates. In order to adsorb on such a surface the reactant molecules must find empty surface sites (active sites) created either by one missing adsorbate (vacancy) or by aggregates (ensembles) of vacancies. In the case of  $H_2$  dissociation on Pd—a process of interest in many industrial reactions, including hydrogenation and fuel cell technologies—a recent scanning tunneling microscopy (STM) study [1] has revealed that the classically assumed mechanism where diatomic molecules require ensembles of two empty sites is too simplistic [1]. Indeed, Mitsui *et al.* [1,2] have found that near saturation coverage the sites for the facile molecular dissociation on Pd(111) require ensembles of three or more H-free nearest neighbors fcc sites. Holloway [3] has suggested that such an unexpected result could be due to chemical self-poisoning of the surface originated by adsorbed hydrogen, further hindering the activity by increasing the dissociation barrier. An alternative mechanism involves the suppression of energy dissipation channels of the exothermic dissociation reaction [3]. This in turn could be due to (a) modification of the  $d$ -band occupation by adsorbed H that would alter the rate of electron-hole pair generation or (b) by surface stiffening, which would reduce phonon excitations. Clearly, the structure and electronic properties of the hydrogen-free ensembles and their effect on the molecular dissociation are fundamental questions that have not been addressed until now.

In this Letter we provide an explanation of the STM observations. In addition, we have been able to determine the detailed structure and geometry of the active ensemble of three sites. Because of the rapid motion of H on the surface, the STM experiments could only determine that the number of sites must be larger than two. The actual geometry of the vacancy ensemble, however, is not directly available. The nonobservation of static (in the

time scale of seconds) sites of three vacancies surrounding an hcp hollow site (labeled  $V_H$ ), however, indicates that this site cannot be the active one in the  $H_2$  dissociation. We show that this is indeed the case and that the active site must contain at least one Pd atom without a direct bond to adsorbed H atoms.

To gain a fundamental understanding of the chemical properties of ensembles of vacancies we carried out density functional theory (DFT) calculations. A standard approach which models the metal surface by periodically repeated slabs of 4 Pd layers separated by six equivalent layers of vacuum is used. Surface coverage ranging from 0 to 1 ML of H is considered. Various configurations of noninteracting vacancies on a  $p(3 \times 3)$  Pd(111) surface are modeled. Hydrogen was adsorbed on one side of the slab with correction for the resulting dipole moment in the vacuum region. Only the adsorbate and the two outermost surface Pd layers have been relaxed. The following systems were employed: (a) fully H-covered surface; (b) surface with separated one H-free site (1V), equivalent to 0.11 ML of vacancies; (c) surface with 0.22 ML of vacancies forming divacancies (2V); and (d) 0.33 ML of vacancies forming a contiguous trimer (3V). Three different trimer configurations are studied: one open ( $3V_O$ ) and two closed configurations ( $3V_H$  and  $3V_T$ ); see Fig. 1. In the  $3V_O$  the vacancies are arranged forming an obtuse triangle whereas in  $3V_H$  and  $3V_T$  the three vacancies form an equilateral triangle centered on either a hcp threefold hollow site ( $3V_H$ ) or on a top Pd site ( $3V_T$ ). A schematic representation of these models is given in Fig. 1. The open  $3V_O$  configuration is shown for completeness but is not used in the rest of the discussion for reasons that will become clear later on. Similar configurations to the ones described above have been observed in the STM experiments. The vacancy aggregation energy, this is the energy required to create dimers or trimers from isolated vacancies, is found to be rather small, Table I. The lifetime of 3V

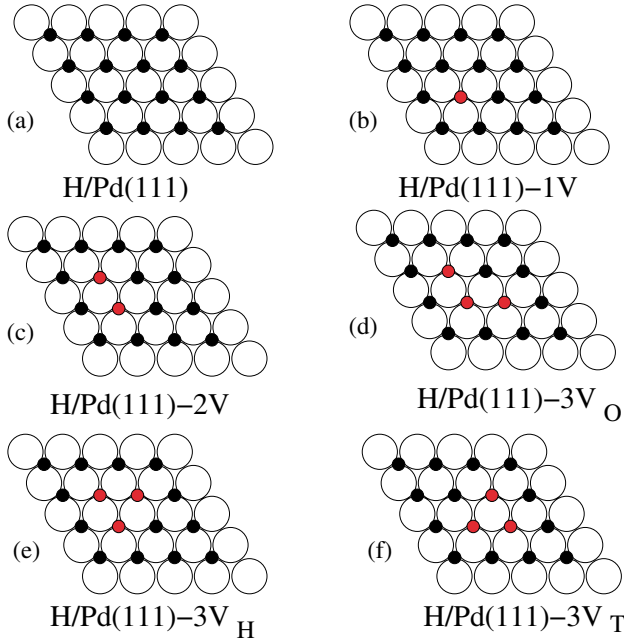


FIG. 1 (color online). Surface models of the H-covered Pd(111) surface with different H-vacancy densities: (a) fully hydrogenated surface; (b) single vacancy (1V); (c) divacancy (2V); (d) open trimer configuration (3V<sub>O</sub>); (e) closed trimer centered around a threefold hollow site (3V<sub>H</sub>); and (f) closed trimer centered around a Pd atom (3V<sub>T</sub>). Palladium atoms are represented by large circles, hydrogen atoms by filled smaller circles and vacancies by small gray (red) circles.

or 2V aggregates is of the order of seconds to minutes in the temperature range investigated, large enough compared to the time scale for hydrogen interacting with the potential well ( $\sim 1$  ms) [2].

The calculations have been performed with the DFT approach as implemented in the VASP code [4]. The ionic cores were described by the projector augmented wave pseudopotentials [5] and the one-electron valence states were expanded in plane waves with kinetic energies up to 315 eV. A Monkhorst-Pack grid of  $4 \times 4 \times 1$   $k$  points was used [6]. Electron densities for the Perdew-Wang (PW91) form of the generalized gradient approximation (GGA) to the exchange-correlation functional [7] were self-consistently determined by iterative diagonalization of the corresponding Kohn-Sham matrix representation of the Hamiltonian. Within this approach the bond energy of H<sub>2</sub> was found to be 4.54 eV, close to the experimental value [8] of 4.75 eV.

For a coverage of  $\theta_H = 0.22$  ML the hydrogen chemisorption energy relative to the H<sub>2</sub> gas reference was found to be  $E_{\text{ads}} = 0.67$  eV per H atom. For  $\theta_H = 0.66$  ML and above the value drops to 0.62 eV, indicating a small coverage dependence. Tests performed with thicker slabs and larger vacuum gaps show that our binding energies per H atom are converged within an error of 0.02 eV. The estimates, however, are larger than the experimental val-

ues,  $E_{\text{ads}} = 0.45$  eV–0.40 eV for low and high coverage, respectively [9,10], reflecting the typical overbinding exhibited by PW91 calculations [11]. Overbinding can be corrected semiempirically by using the experimental ground state energy of H<sub>2</sub> [12]; this leads to an adsorption energy of  $E_{\text{ads}} = 0.56$  eV for clean Pd(111), in good agreement with previous theoretical estimates [12]. However, since our goal is to understand the trends in chemisorption, which are not affected by the definition of the reference energy level, we will consider only the values obtained directly from the calculations without any further correction.

To study the kinetics of hydrogen adsorption on the precovered surface we have explored the reaction paths that lead to adsorption. H atoms adsorbed on fcc sites are the most energetically favored reaction products, therefore adsorption on these sites is investigated. We have explored the minimum energy reaction paths for H<sub>2</sub> dissociation by varying all the H<sub>2</sub> coordinates (the so-called nudged elastic band method [13]). It is found that the results are equivalent to those obtained through a constrained search where the distance from the center of the H<sub>2</sub> molecule to the surface is varied continuously and the molecular axis is kept parallel to the surface [14]. During the approach the H atoms point to empty fcc sites. This search provides a better sampling of the reaction path, and is therefore used in the analysis that follows.

The calculated energy profiles are shown in Fig. 2. A physisorbed molecular state is found separated by a small dissociation barrier from the atomic adsorption state. At high coverage the minimum energy profiles show large variations between different site geometries and composition. The presence of preadsorbed H atoms always destabilizes the physisorbed state. The degree of destabilization depends on the precise local environment, which also affects the magnitude of the energy barriers from the precursor to the dissociated state.

The calculated energy profiles (Fig. 2) allows us to estimate the probability of dissociative chemisorption within the phenomenological Kisliuk model [15], which assumes equilibrium between gas-phase H<sub>2</sub> and weakly adsorbed molecules (the “precursor” state, H<sub>2</sub><sup>\*</sup>). This constitutes a rough estimate of the sticking probability;

TABLE I. Calculated vacancy aggregation energy ( $E_{\text{agg}}$  in eV) dissociative adsorption energies ( $E_{\text{ads}}$  in eV/H atom) and energy barrier ( $E_a$  in eV with respect to the gas phase) of H<sub>2</sub> on Pd(111) for different H coverage ( $\theta_H$ ).

Initial $\theta_H$ /ML	0.88	0.77	0.66	0.66	0
Structure	1V	2V	3V <sub>H</sub>	3V <sub>T</sub>	Pd(111)
$E_{\text{agg}}$	...	0.07	0.13	0.14	...
$E_{\text{ads}}$	...	-0.62	-0.63	-0.63	-0.67
$E_a$	...	0.00	-0.04	-0.12	-0.22

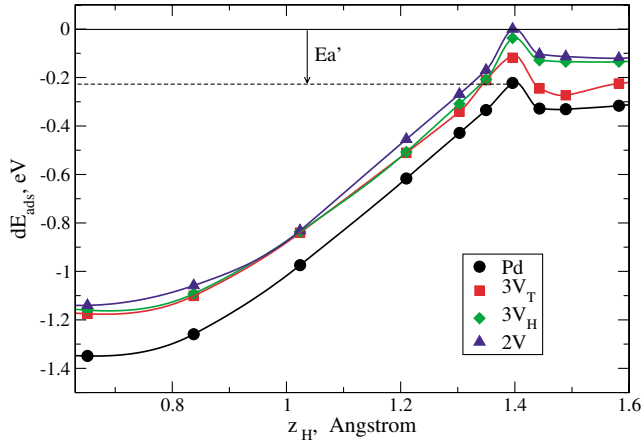
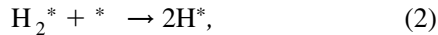


FIG. 2 (color online). Energy profiles for the fcc-fcc hydrogen dissociation pathway at different vacancy structures. The differential heat of adsorption, computed as  $dE_{\text{ads}} = E_{\text{H/Pd}}(NV-2) - E_{\text{H}_2} - E_{\text{H/Pd}}(NV)$ , is plotted as a function of distance to the Pd surface. The molecular axis is parallel to the surface and the 2 H atoms point towards neighboring fcc sites. The gas-phase to chemisorption energy barrier  $E_a'$  is shown for the clean surface case.

see below. The dissociative chemisorption of  $\text{H}_2$  from the precursor is the rate-limiting step of the overall process. The equations for these two steps are then



where  $*$  stands for H-free fcc sites. The rate for the rate-limiting step (2) is

$$r = d\theta_{\text{H}}/dt = 2k_2\theta_{\text{H}_2^*}\theta_* \quad (3)$$

with an Arrhenius rate constant

$$k_2 = A \exp(-E_a/RT), \quad (4)$$

where  $E_a$  is the energy barrier (positive) from the precursor to the dissociated state (right to left in Fig. 2). The equilibrium constant for the reaction (1) can be written as

$$K = \theta_{\text{H}_2^*} p_{\text{H}_2}^0 / (\theta_* p_{\text{H}_2}) = \exp(\Delta E/RT), \quad (5)$$

where  $\Delta E$  is the physisorption energy of  $\text{H}_2$  (positive) and  $p_{\text{H}_2}^0 = 1$  bar. Combining Eqs. (3)–(5) one gets

$$r = 2A \exp(-E_a'/RT) \frac{p_{\text{H}_2}}{p_{\text{H}_2}^0} (\theta_*)^2, \quad (6)$$

where  $E_a' = (E_a - \Delta E)$  is the energy difference between the highest point of the barrier and the reference state (gas-phase  $\text{H}_2$  plus Pd with preadsorbed H).

The dependence of  $E_a'$  on the local configuration of vacancy aggregates can be seen in Fig. 2. Apart from the clean surface, the value of  $E_a'$  for the  $3V_T$  trimer is about 0.1 eV lower than the rest. For the  $3V_H$  configuration the

value of  $E_a'$  is ca.  $\sim 0.04$  eV smaller than that of the  $2V$  structure. This clearly shows that not only the number of vacancy sites in the aggregate, but also their geometrical configuration is important. It is interesting to note that the  $3V_T$  trimer, which offers the best reaction pathway for dissociation, is the only one that contains a Pd atom not directly bonded to an H atom. This clearly points to chemical poisoning as one of the main reasons of the larger activity of  $3V_T$  ensembles. The above analysis refers to the analysis of the minimum energy path through the use of the precursor model and the quasiequilibrium approximation for the first step. However, it is well known that the microscopic behavior of  $\text{H}_2$  on Pd(111) is much more complex, even for the clean surface. At low energies  $\text{H}_2$  steering effects and the dynamical trapping have been identified [16]. A hydrogen precovered surface adds another level of complexity, but details of the microscopic  $\text{H}_2$  dynamics of this process are far beyond the scope of the present Letter and still await solution. Our approach is a first step toward this direction and gives rough quantitative estimation of the relative reaction rates showing the importance of electronic poisoning.

Poisoning effects by preadsorbed atoms due to coverage (amount of atoms) and chemical effects (nature of these adsorbates) have been analyzed in view of the  $d$ -band model [17]. In that case, a single configuration per coverage was studied. The  $d$ -band model [18–20] states that the reactivity of a metal in different environments is controlled by the position of the center of its  $d$  band with respect to the Fermi level. This follows from the fact that adsorbate-surface interaction with the metal  $sp$  band is rather substrate independent and the differential behavior arises from the structure of metal  $d$  band. In the present case, hybridization of  $d$  orbitals with nearby hydrogen stabilizes the metal  $d$  band, shifting it down, away from the Fermi level, and therefore making Pd less reactive. This result is shown in Fig. 3 where the energy

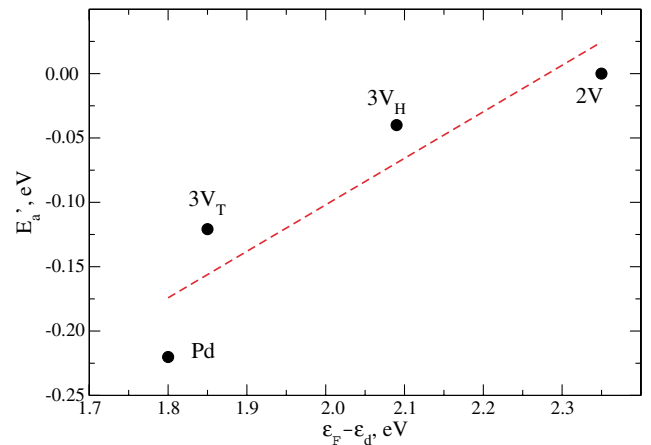


FIG. 3 (color online). Dependence of the activation energy  $E_a'$  on the position of the metal  $d$ -band center with respect to the Fermi level. Energies are referred to the gas-phase  $\text{H}_2$ .

$E_a'$ , is plotted versus the position of the metallic  $d$ -band center.

The conclusions presented above are based on the study of the minimum reaction pathway. However, these results can be extended to other reaction pathways previously analyzed for the clean surface with arguments based on the  $d$ -band model and on the Brønsted-Evans-Polanyi (BEP) relationships [20], where the activation energy for the reaction depends on the adsorption energy of the products. The latter has been shown to be a function on the position of the  $d$  band of the metal [17]. All the reaction paths leading to adsorbed H atoms on different positions at the 2V and 3V<sub>H</sub> vacancy ensembles involve poisoned surface Pd atoms. The chemical poisoning of these centers implies an upwards shift of the barriers for chemisorption in all the possible sites. The shift in the  $d$ -band center due to differences in vacancy configuration (2V, 3V<sub>T</sub>, or 3V<sub>O</sub>) will affect the energy barriers for dissociation to hcp and fcc sites by the same amount. On the 3V<sub>T</sub> configuration the situation is closest to that of clean Pd. There exist several pathways that do not involve poisoned Pd atoms. The values of the barriers for these pathways are ranged in the same order as in the clean surface.

The experimental measurements [1] at 65 K show that on the 3V ensembles the hydrogen sticking coefficient  $s$  is more than 50 times larger than on the 2V ones. The present model gives a reactivity of H-free trimers centered on top positions to be about  $10^9$  times higher than that of the 2V ensembles, and  $10^6$  times higher than that of the 3V<sub>H</sub> ones, and thus explains the experimental observations.

To summarize, the present first principles calculations provide a theoretical understanding of the observation that H<sub>2</sub> dissociation on Pd(111) requires ensembles of at least three empty adjacent fcc sites. According to our calculations, the dissociation site involves not only two empty fcc sites as proposed in the Langmuir model, but also three empty fcc sites in a special configuration where a Pd atom exists that is not directly bound to any adsorbed H atom. H<sub>2</sub> impinging on Pd atoms already bound to H encounter a higher barrier for dissociation due to chemical poisoning. Such results are in agreement with the predictions from the  $d$ -band model. Our results demonstrate also that the concept of “active site” should be refined since these can be ensembles of sites larger and more complex in structure than usually assumed.

This research has been supported by the Spanish DGICYT Grant No. BQU2002-04029-CO2-01 and by

Generalitat de Catalunya Grant No. 2001SGR-00043. N.L. is grateful to MEC for the Ramon y Cajal Grant and F.I. acknowledges the support from Distinció de la Generalitat de Catalunya per a la Promoció de la Recerca Universitària. M.S. acknowledges support from the Director, Office of Science, Office of Basic Energy Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SD00098.

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